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HYDROPURIFICATION OF A REFINED DIESEL OIL

By

R. Sh. Kuliyev and B. A. Sadykhova

FOREIGN TECHNOLOGY DIVISION

AIR FORCE SYSTEMS COMMAND

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HYDROPURIFICATION OF A REFINED DIESEL OIL

R. Sh. Kuliyev and B. A. Sadykhova

A complex of scientific research projects has recently been completed at the Institute of Petrochemical Processes of the Academy of Sciences of the Azerbaidzhan SSR for the purpose of making fundamental improvement in the quality of oils produced at the Baku factories.

The use of the hydrogenation method for additional purification of distillate oils was of particular concern in these projects.

The original distillate of D-11 diesel oil from a mixture of Baku nonparaffinic petroleums and a refined oil obtained by purification of this distillate with 250% furfurol were subjected to hydrogenation.

The present article deals with the results of hydropurification of a refined diesel oil in place of acid-contact repurification.

The hydrogenation was performed in a pilot apparatus with a 200 cm^3 catalyst charge in the reactor and a constant hydrogen flow of 30 liters/hr. The industrial catalysts Al-Co-Mo and WS_2 were used as the catalysts, after the tablets and granules were pulverized to a

crumb size of 1.0-1.5 mm.

The hydropurification was carried out at feed rates of 0.3, 0.5, and 1.0 m^3/m^3 of raw material to the catalyst loaded in the reactor at various temperatures and pressures. The results of experiments conducted with a raw-material supply of 0.5 m^3/m^3 with temperatures in the range from 300-400°C and pressures from 50-200 atm (tech) are described below (Table 1).

TABLE 1

Hydropurification of Refined D-11 Diesel Oil with Al-Co-Mo Catalyst

Conditions of hydropurification		Characteristics of refined oil and purified oil										
Temperature, °C	Pressure, atm(tech)	Density, d_4^{20}	Viscosity at 100°C, cs	Viscosity ratio V_{50}/V_{100}	Viscosity index	Viscosity-weight constant	Acid number, mg/KOH	Coking capacity, %	Flash point in open crucible, °C	Color according to NPA, grade	Corrosion according to Pinkevich method, g/m²	Stability according to the method of the Azerbaidzhan Scientific Research Institute
Original refined oil		0.900	11.20	6.50	60.0	0.840	0.02	0.14	226	dark	—	60
300	50	0.900	11.20	6.50	63.0	0.840	0.02	0.10	220	5	1.90	110
300	100	0.899	11.0	6.40	63.0	0.840	0.02	0.10	220	4 1/2	1.80	118
300	150	0.8965	10.60	6.40	65.0	0.839	0.02	0.08	216	3 1/2	1.00	120
350	50	0.8967	10.93	6.20	66.6	0.8352	0.013	0.010	218	4	—	159
350	100	0.8968	10.57	6.22	68.0	0.8360	0.010	0.040	214	2	—	177
350	150	0.8963	10.54	6.28	68.0	0.8358	0.012	0.050	210	1 1/2	0.540	188
350	200	0.8960	10.52	6.20	68.0	0.8360	0.018	0.048	210	1 1/2	—	190
400	150	0.8919	8.5	5.39	78.0	0.8310	0.01	0.02	150	1 1/2	1.84	161
		0.9000	10.56	6.30	62.0	0.8390	0.02	0.12	225	4 1/2	5.00	230
Oil purified by acid-contact method												

It is apparent from Table 1 that at a temperature of 300°C and a pressure of 50 atm (tech) the quality of the hydropurified oil, in comparison with the original refined oil, is not altered significantly, save for a certain improvement in stability and color.

In comparison with the acid-contact repurification oil, the hydropurified oil is less corrosive and half as stable, as determined by the method of the ASRI.

An increase in pressure to 100 and 150 atm (tech) at a constant temperature of 300°C leads to a certain improvement in the quality of

the refined oil: the viscosity index increases somewhat, and the color improves to a grade of 3 1/2. An increase in the temperature of the hydropurification process from 300° to 350°C at a constant pressure of 50 atm (tech) also leads to a certain improvement in the quality of the refined oil. This oil with respect to all indices, except stabilit. according to the method of the ASRI, surpasses the oil of acid-contact repurification.

The quality of the oil is considerably improved after hydropurification at a pressure of 100 to 150 atm (tech) and a temperature of 350°C.

Oil obtained under these conditions gives the best indices with respect to density, viscosity-weight constant, coking capacity, color, stability, and viscosity index. A further increase in pressure from 150 to 200 atm (tech) has almost no effect on the quality of the refined oil.

An increase in the temperature of the hydropurification to 400°C (cf. Table 1) leads to appreciable destruction of the raw material, as a result of which the viscosity of the refined product is reduced to 8.5 cs, while the flash point is reduced to 150°C.

The results of hydropurification of a refined diesel oil with a WS_2 catalyst are presented in Table 2.

It is apparent from the data in Table 2 that hydropurification of a refined oil in the presence of a WS_2 catalyst proceeds satisfactorily at a temperature of 300°C and a pressure of 50 atm (tech). When the pressure is increased from 50 to 150 atm (tech), the quality of the refined oil is improved. A further increase in the pressure of the process to 200-250 atm (tech) leads to a slight improvement in the qualities of the refined oil.

TABLE 2

Hydropurification of Refined D-11 Diesel Oil with a WS_2 Catalyst

Conditions of hydropurification			Characteristics of refined oil and purified oil											
Temperature, °C	Pressure, atm(tech)	Feed rate of raw material, m^3/m^3	Density, d_4^{20}	Viscosity at 100°C, cs	Viscosity ratio ν_{50}/ν_{100}	Viscosity index	Viscosity-weight constant	Acid number, mg/KOH	Coking capacity, %	Flash point in open crucible, °C	Pour point, °C	Color according to NPA, grade	Corrosion according to Pinkevich method, g/m^2	Stability according to the method of the Azerbaidzhan Scientific Research Institute, min
Original refined oil			0.900	11.20	6.50	60.0	0.840	0.020	0.14	226	−6	Greater than 8	—	50
300	50	0.5	0.900	11.00	6.40	64.0	0.840	0.020	0.050	214	−4	4+	1.60	103
300	100	0.5	0.697	10.90	6.20	65.0	0.839	0.020	0.048	212	−2	3 1/2	1.80	110
300	150	0.5	0.896	10.80	6.20	66.4	0.839	0.020	0.048	212	± 0	2+	1.046	178
300	200	0.5	0.896	10.60	6.10	66.6	0.836	0.015	0.046	210	−2	2+	1.03[illegible]	186
300	250	0.5	0.892	9.50	5.80	68.0	0.836	0.012	0.042	200	−2	2−	—	290
350	100	0.5	0.861	4.30	3.60	100.0	0.810	0.010	0.027	60*	−17	1 1/2	—	—

* Flash point in closed apparatus

Diesel oil obtained by hydropurification of a refined oil with a WS_2 catalyst is not corrosive.

In the case of both the Al-Co-Mo catalyst and the WS_2 catalyst the yield of finished oil was 95%-98% of the original refined oil.

Conclusions

1. Preliminary investigations have established the possibility of replacing contact-acid repurification of a refined diesel oil from a mixture of Baku nonparaffinic petroleums by hydropurification with the industrial catalysts Al-Co-Mo and WS_2.

2. Hydropurification with Al-Co-Mo catalysts at a temperature of 350°C and a pressure of 50 atm (tech) allows us to obtain a diesel oil with somewhat better physicochemical properties than the corresponding oil obtained by repurification of the refined oil with 1% sulfuric acid and 5% clay. Hydropurification carried out at pressures greater than 50 atm (tech) [100-150 atm (tech)] allows us to obtain oils of considerably better quality than acid-contact repurification oils.

3. It has been established that the WS_2 catalyst has a greater hydrogenating capacity than the Al-Co-Mo catalyst. However, an increase in temperature above 300°C leads to cracking in the presence of WS_2.

Institute of Petrochemical Processes
of the Academy of Sciences of the
Azerbaidzhan SSR

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